Contents of the Supplemental Information

Table S-2a. Me/Ca Ratios of Coral 47407B Microsamples.

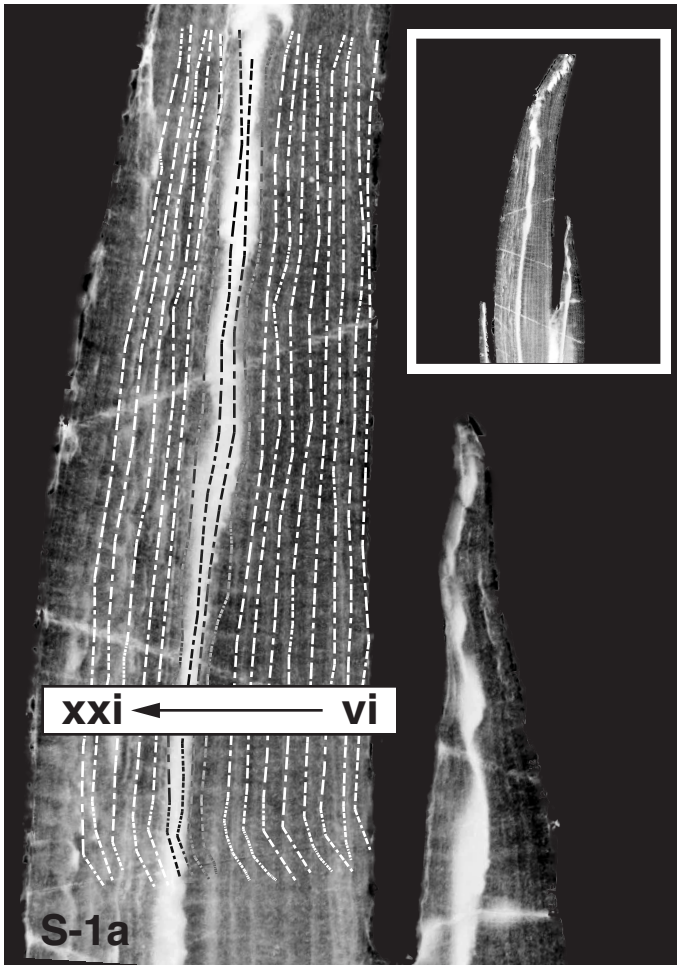
Line ID[a]	sample wt. (μg)	Mg/Ca[b] (mmol/mol)	Sr/Ca[c] (mmol/mol)
vii	117	1.571	10.84
viii	112	1.441	10.76
ix	172	1.400	11.01
x	166	1.420	10.98
xi	125	1.516	10.86
xii	151	1.701	10.48
xiii	126	1.854	10.27
xiv	120	2.675	10.48
xv	92	3.076	10.68
xvi	145	2.398	10.49
xvii	131	1.747	10.17
xviii	145	1.724	10.35
xix	154	1.745	10.41
xx	127	1.619	10.61
xxi	145	1.657	10.76

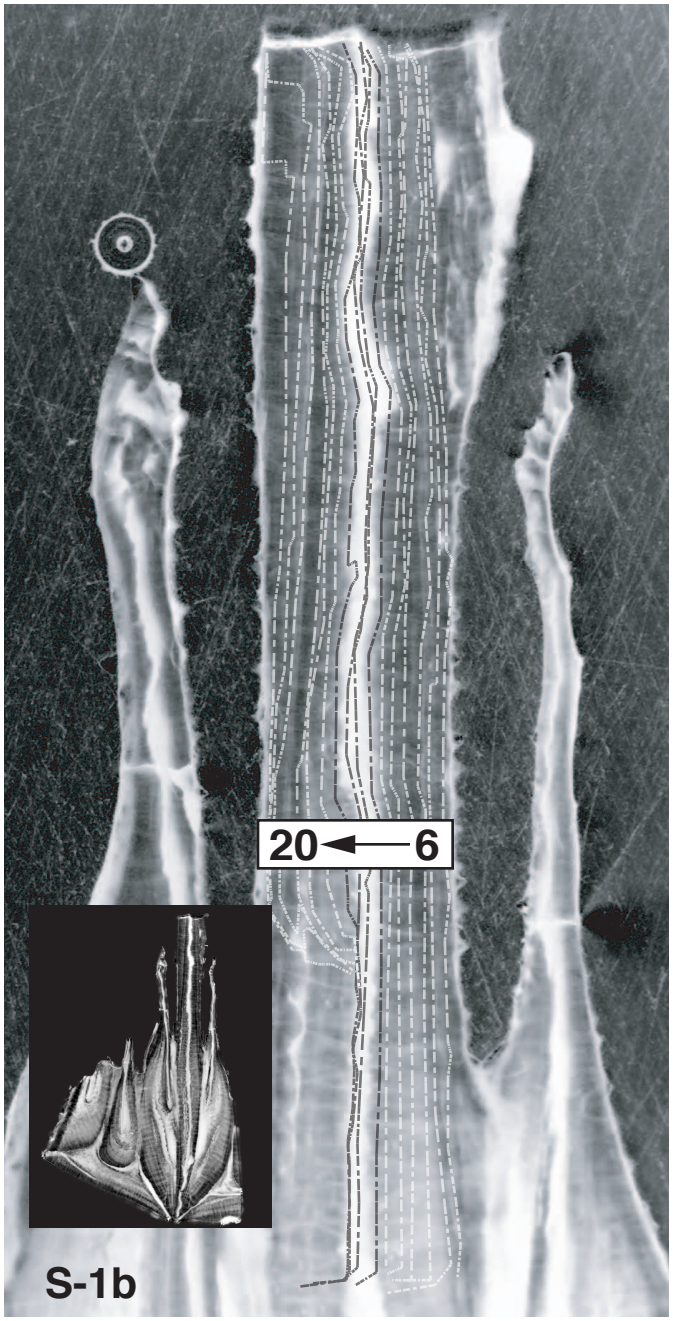
Table S-2b. Me/Ca Ratios of Coral 47407A Microsamples.

Line ID[a]	sample wt. (μg)	Mg/Ca[b] (mmol/mol)	Sr/Ca[c] (mmol/mol)
6	223	1.676	10.56
7	233	1.555	10.49
8	204	1.588	10.57
9	235	1.733	10.55
10	195	1.879	10.47
11	213	2.325	10.55
12	194	2.921	10.63
13	182	3.317	10.66
14	140	2.780	10.74
15	170	2.211	10.62
16	171	1.906	10.47
17	198	1.656	10.70
18	197	1.692	10.49
19	180	1.873	10.55
20	152	1.773	10.35

(a) Line ID refers to sampling described in Fig. S-1.
(b) External reproducibility of Mg/Ca is ± 1.3% (2σ std. dev.).
(c) External reproducibility of Sr/Ca is ± 2.1% (2σ std. dev.).

Fig. S-1. Sampling region of **(a)** 47407B and **(b)** 47407A with dashed vertical lines delimiting successively milled micro-samples. In 47407B, milling lines are labeled successively by roman numerals starting with (vi) on the right, increasing to the left. For coral 47407A, milling lines start at (6) and also increase to the left. These labels correspond to sample numbers in Table S2. Insets in both **(a)** and **(b)** are wide view photomicrographs of the sample showing region of milling.


xxi
vi
S-1a


20
6
S-1b

S3. Metal/Calcium ratios in the presence of active calcium pumping

The balance between the rate of precipitation, p, and active pumping, k, determines the calcium concentration of an otherwise closed solution:

$$\frac{d[\mathrm{Ca}]_{Sol}}{dt} = k - p \qquad \textbf{(S-1)}$$

From the definition for the extent of precipitation, $F \equiv [\mathrm{Ca}]_{Sol}/[\mathrm{Ca}]_O$, and (**S-1**):

$$\frac{dF}{dt} = \frac{(k-p)}{[\mathrm{Ca}]_O} \qquad \textbf{(S-2)}$$

We assume that that both k and p are constant. While this assumption does not take into consideration that the precipitation rate is a function of the solubility product and therefore affected by both $[\mathrm{Ca}]_{Sol}$ and the carbonate system, the simple model developed here is a useful tool for predicting general behavior analytically.

Assuming that calcium is the only species undergoing active pumping, the change in concentration of a trace or minor metal, demonstrated here by strontium, is solely determined by the rate of co-precipitation:

$$\frac{d[\mathrm{Sr}]_{Sol}}{dt} = -pD_{Sr}\left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{Sol} \qquad \textbf{(S-3)}$$

Which can be put in terms of F, the extent of precipitation, by dividing with (**S-2**):

$$\frac{d[\mathrm{Sr}]_{Sol}}{dF} = \frac{d[\mathrm{Sr}]_{Sol}}{dt}\frac{dt}{dF} = \frac{1}{(1-k/p)} D_{Sr}[\mathrm{Sr}]_{Sol}\frac{1}{F} \qquad \textbf{(S-4)}$$

We define ϕ as the term 1/(1-k/p) in (**S-4**) , the balance between precipitation and pumping. Behaving much like an additional partition coefficient, ϕ accounts for changes in $[\mathrm{Ca}]_{Sol}$ affecting all Me/Ca ratios. Separation of the variables $[\mathrm{Sr}]_{Sol}$ and F in (**S-4**),

$$\int \frac{d[Sr]_{Sol}}{[Sr]_{Sol}} = \phi D_{Sr}\int \frac{dF}{F} \qquad \textbf{(S-5)}$$

followed by integration,

$$[\mathrm{Sr}]_{Sol} = [\mathrm{Sr}]_O F^{\phi D_{Sr}} \qquad \textbf{(S-6)}$$

and division with F, yields the Me/Ca behavior of the solution:

$$\left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{Sol} = \left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{\text{intial } Sol} F^{\phi D_{\mathrm{Sr}}-1} \qquad \textbf{(S-7)}$$

To obtain the composition of the instantaneously precipitated solid, the solution Sr/Ca is multiplied by the effective partition coefficient:

$$\left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{Coral} = D_{\mathrm{Sr}}\left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{\text{intial } Sol} F^{\phi D_{\mathrm{Sr}}-1} = \left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{\text{intial Coral}} F^{\phi D_{\mathrm{Sr}}-1} \qquad \textbf{(S-8)}$$

Except for the factor ϕ in the exponential, (**S-7**) and (**S-8**) are identical to the behavior of Sr/Ca in the non-pumping case. Following the derivation developed in the main text, a tracer-tracer relationship in the presence of calcium pumping is linear in a log-log plot, only differing from a completely closed Rayleigh process by the term ϕ:

$$\ln\left(\frac{\mathrm{Sr}}{\mathrm{Ca}}\right)=\left(\frac{\phi D_{\mathrm{Sr}}-1}{\phi D_{\mathrm{Mg}}-1}\right)\ln\left(\frac{\mathrm{Mg}}{\mathrm{Ca}}\right)+\left\{\ln\left(\frac{\mathrm{Sr}}{\mathrm{Ca}}\right)_O-\left(\frac{\phi D_{\mathrm{Sr}}-1}{\phi D_{\mathrm{Mg}}-1}\right)\ln\left(\frac{\mathrm{Mg}}{\mathrm{Ca}}\right)_O\right\} \qquad \textbf{(S-9)}$$

Case 1: Pumping slower than precipitation (*k* < *p*)

If precipitation outpaces calcium pumping, then *k* is less than *p* and ϕ is greater than 1. When D_{Sr} is greater than 1, as expected for aragonite at ocean temperatures, the sign of the slope in the tracer-tracer relationship (**S-9**) will be negative provided $\phi < 1/D_{Mg}$. Using an example from the main text, if D_{Sr} equals 1.25 and a D_{Mg} equals $2.75\text{x}10^{-4}$, Sr/Ca is predicted to decrease with increasing Mg/Ca, the same trend as the completely closed Rayleigh process, provided pumping is less than 99.9% the rate of precipitation.

For *k* less than *p*, pumping tends to accentuate the Rayleigh effect. Me/Ca ratios change with *F* at a faster rate in the presence of pumping compared to its absence. If the effective partition coefficients differ significantly between two tracers, this effect will tend to steepen the slope of the tracer-tracer relationship as pumping increases.

Case 2: Pumping outpaces precipitation (*k* > *p*)

If *k* is greater than *p*, then ϕ is negative and the slope of the tracer-tracer relationship (**S-9**) is always positive. Since pumping cannot be balanced by precipitation, $[\mathrm{Ca}]_{Sol}$ and *F* increase while all Me/Ca ratios decrease.

Case 3: Steady-State Calcium Concentration (*k* = *p*)

If pumping and precipitation are balanced, then $[\mathrm{Ca}]_{Sol}$ remains unchanged at a steady-state value. As coprecipitation occurs, Me/Ca ratios will decrease with time regardless of the value of the effective partition coefficient:

$$\left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{Sol}=\left(\frac{[\mathrm{Sr}]}{[\mathrm{Ca}]}\right)_{\text{intial }Sol} e^{-D_{Sr}\frac{p}{[\mathrm{Ca}]}t} \qquad \textbf{(S-10)}$$

The tracer-tracer relationship is log-log linear but will always have a positive slope

$$\ln\left(\frac{\mathrm{Sr}}{\mathrm{Ca}}\right)=\frac{D_{\mathrm{Sr}}}{D_{\mathrm{Mg}}}\ln\left(\frac{\mathrm{Mg}}{\mathrm{Ca}}\right)+\left\{\ln\left(\frac{\mathrm{Sr}}{\mathrm{Ca}}\right)_O-\frac{D_{\mathrm{Sr}}}{D_{\mathrm{Mg}}}\ln\left(\frac{\mathrm{Mg}}{\mathrm{Ca}}\right)_O\right\} \qquad \textbf{(S-11)}$$

In the steady-state case, Sr/Ca is predicted to decrease with decreasing Mg/Ca. Since D_{Mg} is much less than D_{Sr}, this scenario predicts a very large positive slope.

Case 1 is the only scenario considered here that predicts an inverse relationship between Sr/Ca and Mg/Ca.